Energy Gap in Superconducting Fullerides: Optical and Tunneling Studies

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Tunneling and optical transmission studies have been performed on superconducting samples of Rb_3C_{60}. At temperatures much below the superconducting transition temperature T_c, the energy gap is $2\Delta = 5.2 \pm 0.2$ meV, corresponding to $2\Delta/k_B T_c = 4.2$. The low temperature density of states and the temperature dependence of the optical conductivity resemble BCS behavior, although there is an enhanced "normal state" contribution. The results indicate that this fulleride material is an *s*-wave superconductor, but the superconductivity cannot be described in the weak coupling limit. [S0031-9007(96)01588-8]

The symmetry of the order parameter and the magnitude of the energy gap are two of the most fundamental properties of superconductors. While there is general agreement about the *s*-wave nature of superconductivity in the alkali metal fulleride compounds, the magnitude of the energy gap is not known with sufficient accuracy.

Why is the determination of the energy gap so important? Let us consider, for example, the Eliashberg theory of phonon-mediated superconductivity, and represent the phonons by a single Einstein mode [1,2]. There are two parameters in this theory: the phonon frequency ω_0 and the coupling between electrons and phonons λ. (The latter one may be viewed as an "effective" electron-phonon coupling constant, incorporating the "true" λ and the electron-electron repulsion parameter μ [1,3].) In the weak coupling (BCS) limit the quantity $\omega_0 \exp(-1/\lambda)$ is the only relevant combination of parameters. In that limit the ratio of the low temperature value of the superconducting energy gap to the critical temperature is always $2\Delta/k_B T_c = 3.53$. If the coupling is strong, however, knowledge of the critical temperature and the low temperature gap provides us with λ and ω_0. Once the magnitudes of these parameters are known, theoretical models for the microscopic mechanism of superconductivity [4] can be placed in the proper context.

A review of the literature reveals a great disparity between the various measurements of the superconducting energy gap in Rb_3C_{60}. Direct spectroscopic methods to determine the gap include optical spectroscopy, tunneling, and photoemission. The first optical study by Rotter *et al.* [5] resulted in values of $\eta \equiv 2\Delta/k_B T_c \approx 3-4$. Fitzgerald *et al.* [6] obtained $\eta \approx 3-5$ from transmission measurements on thin film samples. In more recent reflectance measurements on polycrystalline [7] and single crystal [8] samples, Degiorgi *et al.* obtained $\eta \approx 2.98$ and $\eta \approx 3.45$, respectively. Zhang *et al.* [9] reported tunneling measurements yielding a value greater than 5, whereas Jess and coworkers measured values between 2 and 4 in a STM study [10]. Photoemission experiments by the Argonne-University of Illinois collaboration [11] led to $\eta \approx 4.1 \pm 0.4$. Nuclear magnetic resonance [12,13] and muon spin relaxation [14] yielded values compatible with the BCS weak coupling limit. (All numerical values summarized here apply to Rb_3C_{60}.)

An accurate determination of η and the detailed fit of the theoretical curves to the experimental results answer a fundamental question: Is the coupling between the electrons weak enough for the BCS theory to describe superconductivity? In this Letter we report optical transmission and tunneling measurements unambiguously demonstrating that the ratio $2\Delta/k_B T_c$ is 4.2 ± 0.2, significantly larger than the BCS value. Since the weak coupling conditions are not satisfied, we are able to deduce the phonon coupling constant and the characteristic phonon frequency, obtaining $\lambda = 0.9$ and $\omega_0 = 210$ cm^{-1} ($\hbar\omega_0 = 26$ meV). The electron-phonon coupling is consistent with the value determined from dc resistivity measurements [15]; the phonon frequency is close to the lowest lying Raman frequency of the C_{60} molecule [16].

The pressed pellet samples for the tunneling measurements were made by heating and mixing stoichiometric amounts of Rb and C_{60} in a quartz tube for several weeks. According to powder x-ray diffraction, the sample contained no secondary phases. The material was pressed into a pellet, with four gold wires embedded for electrical contacts. The resistivity as a function of the temperature is shown in Fig. 1. The resistivity of the pressed pellet sample was as low as the resistivity of single crystals [15]. The superconducting transition temperature was 30 K.

The optical measurements were performed on samples prepared by deposition of a thin C_{60} film on a Si substrate and subsequent exposure to Rb vapor in a sample cell mounted in a Bomem MB-155 spectrometer [17]. The composition of the sample was monitored by observing
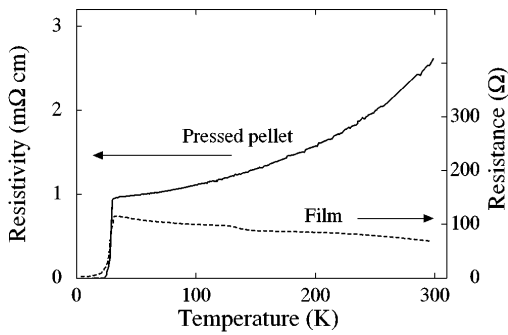
FIG. 1. Resistivity and resistance of the thin film and pressed pellet samples used in the optical and tunneling measurements, respectively.

the $F_{1u}(4)$ vibrational mode of the C_{60} molecule [18]. The thickness of the film was 1.0 ± 0.1 μm. Scanning force microscope images of the sample surface showed an irregular surface with poorly matching crystal faces. From room temperature to 30 K there was a factor of 2 increase of resistance, typical of thin film samples [19] and indicative of granular morphology (Fig. 1). The superconducting transition occurred at 30 K; a smearing of the transition suggested a distribution of critical temperatures, also consistent with granular morphology.

The far-IR transmission spectra were measured as a function of temperature at the U4IR beam line of the National Synchrotron Light Source at Brookhaven National Laboratory. The sample cell was mounted on a Helitran He flow refrigerator, and the spectra were taken in a Nicolet 20F Rapid Scan Fourier-transform infrared (FTIR) spectrometer. Because of the capacitive intergrain coupling, ac measurements (including the optical transmission) are expected to be less sensitive to the grain boundaries than the dc transport. In accordance with this expectation, the optical transmission of the film decreased upon cooling, corresponding to the increasing intrinsic conductivity of the crystallites.

The upper panel in Fig. 2 shows the low temperature transmission results, normalized to the spectrum taken in the normal state at 35 K. The pronounced peak in the optical transmission is direct evidence for the sharp energy gap in the real part of the optical conductivity at $\hbar\omega = 2\Delta$. This feature was first observed for superconductors, and discussed in detail, by Glover and Tinkham [20].

Calculated transmission curves are shown in the lower panel of Fig. 2. In the absence of readily available Eliashberg results for the density of states and optical conductivity, we modified the BCS result [21] to include the effects of inelastic pair breaking [22] in a phenomenological way. The total optical transmission t was represented in a two component model, in the form of $t = wt_{sc} + (1 - w)t_n$, where t_n is the transmissions of a Drude metal, and t_{sc} was calculated from the Mattis-Bardeen [21] conductivity of a superconductor. This approach also accounts for the inevitable imperfections in the sample. In the best fits the
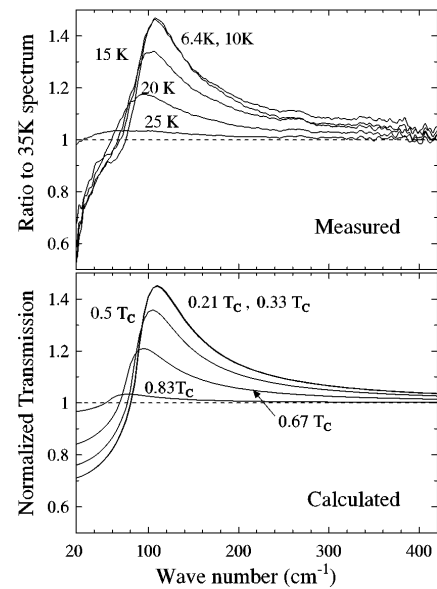

FIG. 2. (top) Far infrared transmission of the sample at temperatures below the superconducting transition. The curves are normalized to the transmission at $T = 35$ K in order to eliminate the features due to the silicon substrate. (bottom) Calculated transmission curves, based on dirty limit BCS results.

weight factor was about $w = 30\%$ at the lowest temperature, and it decreased as the temperature approached T_c. The energy gap as a function of the temperature, evaluated from these fits, is shown in Fig. 3. Notice that the energy gap at zero temperature corresponds to $\eta \approx 4.1 \pm 0.2$. For comparison, the temperature dependence of the weak coupling (BCS) gap, scaled to $2\Delta = 4.1 k_B T_c$, is also shown in the figure.

For the tunneling measurements the pressed pellets were first cooled to low temperature. A break junction was made and controlled by mechanical means. The device was similar to the one used in the tunneling studies of high T_c superconductors [23]. The sample was in He atmosphere to prevent the degradation of the material due
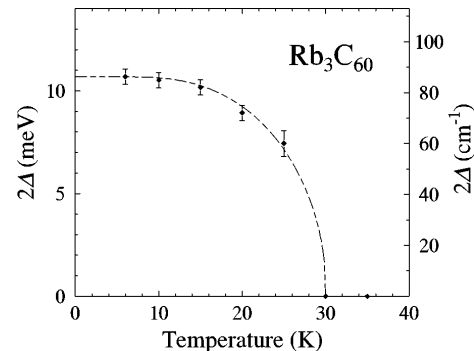

FIG. 3. Temperature dependence of the energy gap evaluated from the optical transmission data. The dashed line represents the BCS temperature dependence, scaled to satisfy $2\Delta = 4.1 k_B T_c$.

to the chemical reaction with oxygen. The differential conductance of a typical junction at $T = 4.2$ K is shown in Fig. 4. The poor thermal stability of the junction prevented us from measuring the temperature dependence of the tunneling.

Ideal break junctions are superconductor-insulator-superconductor (SIS) junctions. The tunneling current is described by $I \propto \int gfg'f'dE$, where $g = g(E)$ and $g' = g(E - eV)$ are the densities of states and $f = f(E)$ and $f' = f(E - eV)$ are Fermi functions [24]. The simple BCS density of states is often modified to

$$g(E) \approx \left| \mathrm{Re} \, \frac{E + i\delta}{\sqrt{(E + i\delta)^2 + \Delta^2}} \right|, \quad (1)$$

where the phenomenological parameter δ accounts for the pair breaking effects [22,25]. The continuous line in Fig. 4 was obtained by adjusting Δ, δ, and the vertical scale factor of the differential conductance. Apart from the elevated zero bias conductance and the upturn of conductivity at larger bias voltages, the agreement is satisfactory. (The parameters are $2\Delta \approx 5.2$ meV and $\delta \approx 1.5$ meV). A more complete calculation, including an additional leakage conductance at zero bias and a voltage dependent tunneling rate [26], results in an even better fit (dashed line). Most importantly, the figure demonstrates that the value of the energy gap is not sensitive to the processing of the data: The peak position of the raw data and the two fitting procedures yield $2\Delta \approx 5.2$ meV, corresponding to $\eta \approx 4.3 \pm 0.2$.

The accuracy of the results and the agreement between the two principal spectroscopic methods (optics and tunneling) leave little doubt about the magnitude of the low temperate energy gap in Rb_3C_{60}. The ratio
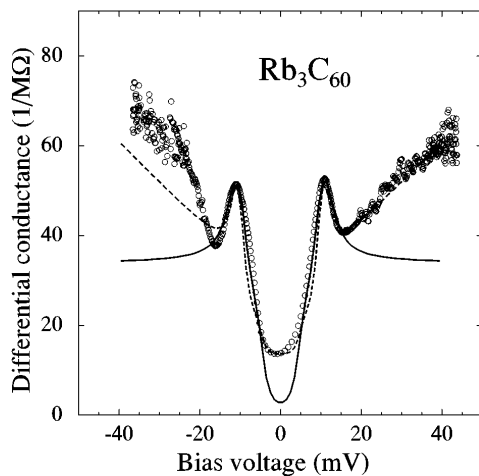

FIG. 4. Differential conductance of the break junction made of a polycrystalline RbC_{60} pellet (open circles). The continuous line is a three parameter fit using a modified BCS formula for the density of states (see text). The dashed line was obtained by including an additional leakage conductance at zero bias and the voltage dependence of the transmission function of the junction.

$\eta \equiv 2\Delta/k_B T_c \approx 4.2 \pm 0.2$ is obtained, which is clearly beyond the weak coupling value. This result is compatible with, although more accurate than, most of the earlier spectroscopic studies [27], and it agrees particularly well with the photoemission study [11]. Thus all three direct methods (tunneling, optics, and photoemission) yield very similar values.

In early NMR measurements the absence of the Hebel-Slichter (H-S) peak in the relaxation rate was interpreted as evidence for strong coupling [12,28]. More recently, Stenger et al. [13] observed the H-S peak and argued that Rb_3C_{60} is in the weak coupling regime. In particular, $\eta \approx 4.8$ was excluded as too high. However, due to the many factors influencing the magnitude of the H-S peak, smaller values of η could not be excluded. Interestingly, Stenger et al. puts a lower bound of 200 cm^{-1} on the phonon frequency, and our result is entirely compatible with that constraint.

Kiefl et al. determined $\eta \approx 3.6 \pm 0.3$ from muon spin rotation experiments. The interpretation of the results is similar to the NMR relaxation rate, except the low temperature limiting behavior is more accessible with muons. The spin relaxation rate depends on the number of electrons in the conduction band. For BCS superconductors these electrons are thermally activated, thus the relaxation rates should exhibit Arrhenius temperature dependence at low T. This straightforward interpretation becomes rather complicated for intermediate and strong coupling. At finite temperatures, the density of states is nonzero at the Fermi level (unlike the BCS limit) [22]. Indeed, Kiefl et al. used a broadened density of states, such as described in Eq. (1). The value of the gap depends on the assumptions made for the temperature dependence of δ. We believe that, in this case, it is crucial to use the full Eliashberg calculation to obtain a more reliable value for Δ. Notice the contrast to the direct spectroscopic studies, where the phenomenological parameter δ does not influence the numerical magnitude of the gap in any significant way.

The dimensionless electron-phonon coupling constant and the characteristic phonon frequency can be determined as follows. According to Carbotte [2], for various superconductors, η can be well approximated by

$$\eta \approx 3.53 \left[1 + 12.5 \left(\frac{k_B T_c}{\hbar \omega_0} \right)^2 \ln \frac{\hbar \omega_0}{2 k_B T_c} \right]. \quad (2)$$

Here ω_0 is related to the Eliashberg spectral density $\alpha^2 F$ by $\ln \omega_0 = (2/\lambda) \int_0^\infty \ln(\omega) \alpha^2 F/\omega d\omega$ and $\lambda = \int_0^\infty \alpha^2 F/\omega d\omega$ [1,2]. The η value determined here corresponds to $T_c/\omega_0 = 0.10$. This, in turn, leads to the dimensionless coupling constant of $\lambda = 0.89$ [from Eq. (2) of Allen and Dynes [1]] or a slightly larger value if the repulsive electron-electron interaction is also considered (one obtains, for example, $\lambda = 1.16$ for $\mu = 0.1$).

Two important conclusions can be drawn from our results. First, the coupling constant is reasonably close

to the $\lambda_{tr} \approx 0.65-0.80$, obtained from the dc electrical transport measurements by Vareka and Zettl [15]. Notice that, for most BCS superconductors, λ and λ_{tr} are close, but the two quantities do not have to be equal [29]. This agreement makes Rb_3C_{60} look like one of the most simplistic materials. We have to keep in mind, however, that with $\lambda_{tr} \approx 1$ the mean free path of the electrons is actually shorter than the lattice spacing. The existence of metallic conduction with such a short mean free path remains one of the mysteries of the transport in alkali fullerides.

The second conclusion concerns the characteristic phonon frequency. It turns out to be $\omega_0 \approx 210$ cm^{-1}, which is larger than the typical frequency of the acoustic phonons. This result is in agreement with the photoemission studies and calculations of Gunnarson et al. [4], where the low-lying Raman modes of the C_{60} molecule proved to contribute significantly to the electron-phonon coupling.

In summary, we investigated the energy gap of the superconducting state of Rb_3C_{60}, and we demonstrated that this material cannot be described by the (weak coupling) BCS theory. The dimensionless electron-phonon coupling constant and the typical phonon frequency were determined. It is expected that the Eliashberg theory, with a coupling constant in the order of 1, fully describes the superconductivity of this material.

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